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(54) Title: **GLASS ADHESIVE AND ARTICLE TO BE ADHERED TO GLASS**

(57) Abstract: To provide an adhesive for glass, which is particularly suitable for adhering an article to a glass surface as an adhering surface, exhibits good slidability without the use of detackifying particles, and has removal cleanliness after the completion of adhesion. An adhesive for glass which is used to be press adhered to a glass surface as an adherent, which contains polycaprolactone and a crosslinked tackifying polymer obtained by polymerizing a monomer mixture containing a monomer having a hydroxyl group in the molecule, a monomer having a phenyl group in the molecule, and a monomer having a C4-C10 alkyl group in the molecule.

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## GLASS ADHESIVE AND ARTICLE TO BE ADHERED TO GLASS

### Field of the Invention

5           The present invention relates to an adhesive for glass comprising a tackifying polymer and polycaprolactone.

### Background of the Invention

10           Some publications disclose adhesives comprising a tackifying polymer having pressure-sensitive adhesion properties, and polycaprolactone in combination.

          For example, US-A-5,192,612 (=JP-B-3021646) discloses a pressure-sensitive composition comprising a pressure-sensitive adhesive base resin (a tackifying polymer such as an acrylic polymer), a detackifying resin and a detackifying particulate. A specific preferable example of the detackifying resin is substantially linear polycaprolactone  
15           having a molecular weight of about 3,000 to about 342,000. Polycaprolactone is a crystalline polymer which exhibits non-tackifying properties at room temperature (about 15 to 30°C).

          The above-described pressure-sensitive adhesive can be adhered to an adherent by pressing the adhesive against the adherent. The above detackifying resin and the  
20           detackifying particles effectively reduce tack on the surface of the adhesive at room temperature and improves repeelability. The repeelability means that an adhesive material can be adhered, peeled, readhered and repeeled, and the positioning or the position-adjustment is easy prior to the final adhesion. In this art field, the repeeling properties are also known as "repositionability", "slidability" (ease of sliding) or the like. The amount of  
25           the pressure sensitive adhesive base resin contained in the above pressure sensitive adhesive is preferably from 55 to 98 wt. %, while that of the detackifying resin is preferably from 1 to 30 wt. %, based on the entire weight of the adhesive. Furthermore, the amount of the detackifying particles is preferably from 1 to 15 wt. % based on the entire weight of the adhesive. However, it is not supposed that the adhesive is peeled off  
30           from the adherent during or after the use, once the adhesive is finally adhered to the adherent.

          In the meantime, adhesives having the improved repeeling properties, which are not the combination of polycaprolactone and a tackifying polymer, are disclosed other

publication, for example, US-A-5,648,425, US-A-5,552,451, etc., and it is understood that the repeeling property is one of the useful properties required for adhesives.

JP-A-2000-119624 discloses a heat-activation adhesive comprising a specific tackifying polymer and a polyester such as polycaprolactone, etc. Using the disclosed adhesive, an article such as an electronic part or a polymer film can be adhered to an adherent by heat pressing. Polycaprolactone efficiently functions as a thermoplastic polymer, and the combination of polycaprolactone and the tackifying polymer having good compatibility with polycaprolactone can form a heat-activation adhesive having improved adhesion strength. The disclosed adhesive has good slidability since it has substantially no surface tack prior to heating.

In this JP publication, a polymer obtained by polymerizing a monomer mixture containing (A) a monomer having a hydroxyl group in the molecule and (B) a monomer having a phenyl group in the molecule is disclosed as a preferable tackifying polymer having good compatibility with polycaprolactone. Such a polymer has two functional groups, that is, the hydroxyl group and the phenyl group, as the essential functional groups in the molecule, and the functions of these functional groups improve the compatibility with polycaprolactone. However, this JP publication does not suggest that such a heat-activation adhesive is used to adhere an article to an adhering surface consisting of a glass surface by press adhering.

Although there is no relationship with the slidability, a pressure sensitive adhesive disclosed in US-A-5,412,035 (= JP-A-6-510548) is one of the prior art adhesives.

The disclosed pressure sensitive adhesive becomes pressure sensitive at least at one temperature in the range between 20°C and 40°C, and comprises a polymeric pressure-sensitive adhesive component and a crystalline polymer. The crystalline polymer is usually non-tacky at room temperature and has good affinity with the polymeric pressure-sensitive adhesive component, and it is intimately mixed with the polymeric pressure-sensitive adhesive component.

The melting point  $T_a$  (°C) of the crystalline polymer, which is measured in the adhesive, is lower than the melting point  $T_m$  (°C) of the crystalline polymer as such, and the difference  $T_m - T_a$  is preferably from 1°C to 9°C. That is, the disclosed adhesive is an adhesive having easy thermal repeelability, that is, a peel strength  $P_2$  (g/cm) at a certain

temperature higher than  $T_a$  is smaller than a peel strength  $P_1$  (g/cm) at a certain temperature lower than  $T_a$ .

However, this US patent does not disclose the improvement of the slidability or the use of polycaprolactone as a crystalline polymer. Furthermore, the US patent does not  
5 disclose a "thermal-peeling-easy" adhesive, which is effective with the glass surface.

### Summary of the Invention

General adhesives are more easily adhered to the glass surface than to the adhering surfaces of other materials, and it is difficult to increase the adhesion strength (peel  
10 strength) of the general adhesives while maintaining the good slidability. One of the reason may be that the glass surface has very good surface smoothness in comparison to the adhering surfaces of other materials. Thus, the inclusion of the detackifying particles such as silica particles as disclosed in US-A-5,192,612 is one of the advantageous methods. However, adhesives containing silica particles are not preferable for the  
15 application on an adhering surface such as the glass surface, which is easily scratched, since the silica particles are hard enough to be used as adhesives.

Sometimes, articles such as adhesive sheets or parts should be removed from the adherents, after they are used for a relatively long time (several months or longer). When the articles are removed from the adherents after the long time use, the adhesive layer is  
20 cohesively failed, so that the adhesive layer is often left on the adherent. Such adhesive leavings should be prevented in any applications.

However, US-A-5,192,612 does not disclose any means to improve a property that an adhesive can be peeled off from the glass surface with no adhesive leavings after the adhesion is completed, that is, removal cleanliness, although it discloses the improvement  
25 of the repeeling properties at the time of adhering.

Thus, one object of the present invention is to provide an adhesive for glass, which is particularly suitable for adhering an article to a glass surface as an adhering surface, exhibits good slidability without the use of detackifying particles, and has removal cleanliness after the completion of adhesion.

30 To solve the above problems, the present invention provides adhesive for glass which is used to be press adhered to a glass surface as an adherent comprising a

crosslinked tackifying polymer and polycaprolactone, characterized in that said tackifying polymer is a polymer obtained by polymerizing a monomer mixture containing

- (a) a monomer having a hydroxyl group in the molecule,
- (b) a monomer having a phenyl group in the molecule,

5 and

- (c) a monomer having a C<sub>4</sub>-C<sub>10</sub> alkyl group in the molecule.

The adhesive of the present invention is placed between an article (e.g. a sheet substrate, etc.) and a glass surface as an adhering surface, and pressed against the adhering surface so that the adhesive is press adhered to the adhering surface. In general, such a press  
10 adhering operation can be performed without heating the adhesive. Such an adhesive is particularly useful as an adhesive to be contained in an adhesive layer of an adhesive sheet which is adhered to the glass surface.

#### Description of the Preferred Embodiment(s)

##### 15 Adhesive for glass

The adhesive for glass according to the present invention is characterized in that it comprises a specific tackifying polymer and polycaprolactone.

The tackifying polymer used in the present invention is a polymer obtained by polymerizing a monomer mixture containing (a) a monomer having a hydroxyl group in  
20 the molecule, (b) a monomer having a phenyl group in the molecule and (b) a monomer having a C<sub>4</sub>-C<sub>10</sub> alkyl group in the molecule.

The tackifying polymer functions to improve the property of the adhesive such that the adhesive is easily adhered to the glass surface by pressing the adhesive to the glass surface, that is, the press adhering property against glass. Polycaprolactone functions to  
25 improve the slidability with the glass surface, and removal cleanliness.

In the molecules of the tackifying polymer, the recurring units derived from the monomer (c) mainly function to improve the press adhesion properties against glass.

When the number of carbon atoms in the alkyl group of the monomer (c) is less than 4, the adhesion properties of the tackifying polymer against glass deteriorates and  
30 thus the adhesion properties of the adhesive as a whole against glass deteriorates. When the number of carbon atoms in the alkyl group exceeds 10, the affinity and compatibility of the tackifying polymer with polycaprolactone tend to decrease. When the affinity and

compatibility with polycaprolactone decrease, the slidability against glass or the thermally easy-peeling properties, which are explained in detail later, deteriorate. In view of the increase of light transmission of the adhesive, the decrease of the compatibility is disadvantageous.

5           The recurring units derived from the components (a) and (b) function to improve the affinity and compatibility of the tackifying polymer with polycaprolactone.

Accordingly, the monomers (a) and (b) are preferably contained in the monomer mixture in an amount not less than a certain lower limit. On the other hand, they are preferably contained in the monomer mixture in an amount not exceeding a certain upper limit, so  
10       that the adhesion properties of the adhesive polymer to the glass are not impaired.

Therefore, the amount of each monomer is preferably determined so that the above functions and the properties and performances of the adhesive are improved in good balance. In general, the total amount of the monomers (a) and (b) is from 42 to 90 wt. %, while the amount of the monomer (c) is from 9 to 55 wt. %, based on the whole weight of  
15       the monomer mixture.

To further improve the above functions and the properties and performances of the adhesive, the amounts of the monomers are determined by further taking the balance of the monomer amounts into consideration. That is, the total amount of the monomers (a) and (b) is preferably from 43 to 80 wt. %, in particular from 44 to 75 wt. %, while the amount  
20       of the monomer (c) is preferably from 18 to 55 wt. %, in particular from 20 to 52 wt. %, based on the whole weight of the monomer mixture.

In general, the content of the tackifying polymer is from 55 to 97 wt. % based on the whole weight of the adhesive, while the content of polycaprolactone is from 2 to 44 wt. %.

25           When the content of the tackifying polymer is too low, the press adhering properties against glass deteriorate and thus the peel strength after the completion of the adhesion cannot be increased to a useful level (at least 8 N/25 mm in the 180 degrees peeling test). The adhesive of the present invention can be adhered to the glass surface by simply pressing it to the glass at room temperature (about 15 to 30°C). To increase the  
30       slidability against the glass surface and the removal cleanliness, the content of the tackifying polymer is preferably 97 wt. % or less.

Polycaprolactone functions to increase the slidability against the glass surface and the removal cleanliness, as described above. To surely attain such effects, the content of polycaprolactone is preferably at least 2 wt. %. On the other hand, to avoid the deterioration of the press adhering properties against glass of the whole adhesive, the content of polycaprolactone preferably does not exceed 44 wt. %.

To further increase the above functions and the properties and performances of the adhesive, the amounts of the components are preferably determined by taking the balance of the amounts of the components into consideration. Thus, the content of the tackifying polymer is preferably from 59 to 96 wt. %, in particular from 65 to 95 wt. %, and the content of polycaprolactone is preferably from 3 to 40 wt. %, in particular from 4 to 34 wt. %, based on the whole weight of the adhesive.

Preferably, the contents of the tackifying polymer and polycaprolactone are selected from the above ranges to increase the thermal-easy-peeling properties, that is, the properties making it easy to peel off an article from an adherent by heating after the long time use, which are explained below.

As explained in the above, the tackifying polymer should have good compatibility and affinity with polycaprolactone. Preferably, the tackifying polymer is compatible with polycaprolactone at a temperature not lower than the melting point of polycaprolactone, the details of which are explained below.

Another characteristic of the adhesive for glass according to the present invention is that the tackifying polymer compatible with polycaprolactone is crosslinked. The crosslinking of the tackifying polymer contributes to the increase of the removal cleanliness. Since the cohesive force is effectively increased by crosslinking, the leaving of the tackifying polymer on the adherent is prevented when the adhesive is removed from the adherent.

Since polycaprolactone is intimately mixed with the crosslinked tackifying polymer, the removal cleanliness of the adhesive as a whole can be improved. In addition, it is advantageous that the crosslinking of polycaprolactone, which will prevent the melting and recrystallization of polycaprolactone, is not necessary when the thermal peeling operation is required.

When the tackifying polymer is compatible with polycaprolactone at a temperature not lower than the melting point of polycaprolactone, the adhesive functions as an

adhesive for glass having the thermal-easy-peeling properties. That is, in one preferred embodiment, the present invention provides an adhesive for glass having the thermal-easy-peeling properties,

(1) which achieves the easily peelable state by heating it to a specific temperature  
5 to decrease the peel strength to a value smaller than that prior to heating, on a desired occasion,

(2) which can maintain and extend such an easily peelable state to a certain period of time,

(3) which has removal cleanliness so that it can be peeled off without leaving the  
10 adhesive on the adherent in the thermal peeling operation,  
and

(4) which has improved readhering properties so that it can be easily readhered to an adherent after peeling.

Polycaprolactone easily melts when it is heated to a temperature not lower than its  
15 melting point and becomes compatible with the tackifying polymer so that it increases the peeling easiness. Furthermore, since polycaprolactone is a non-tacky polymer, it effectively increases the removal cleanliness even when the adhesive is thermally peeled off. In addition, since the tackifying polymer is compatible with molten polycaprolactone, the crystallization of polycaprolactone after heating (recrystallization) can be retarded.

20 The melting and recrystallization of polycaprolactone in the adhesive are substantially reversible physical changes (phenomena). Thus, the adhesive can restore substantially the same state as that prior to heating, when and after it is readhered subsequent to the heating of the composition. Accordingly, the adhesive can be readhered in the same way as the first adhering. Furthermore, the composition can be again peeled  
25 off by heating after it is readhered.

From such a viewpoint, it is preferable to use a crosslinking component which does not substantially chemically react with polycaprolactone, when the adhesive further comprises a crosslinking component (crosslinking agent). Since polycaprolactone usually has hydroxyl groups at both polymer chain ends, the tackifying polymer preferably has a  
30 functional group other than hydroxyl groups (e.g. a carboxyl group, etc.) as a crosslinkable functional group reactive with the crosslinking component in the molecule.



When the adhesive further comprises the crosslinking component, the monomer mixture preferably comprises (D) a monomer having a crosslinkable functional group reactive with the crosslinking component. Thereby, the tackifying polymer is crosslinked through the reaction of the crosslinking component and the crosslinkable functional group.

5 Accordingly, the cohesive force of the adhesive as a whole is effectively increased without crosslinking polycaprolactone, and the removal cleanliness is improved. Such a functional group and such a crosslinking component will be explained in detail.

When the adhesive of the present invention is used to adhere a transparent film or sheet to a pane, preferably the transparency of the adhesive is increased as much as possible. In such a case, the content of polycaprolactone is usually 30 wt. % or less, 10 preferably 25 wt. % or less, more preferably 2 to 20 wt. %, based on the whole weight of the adhesive.

#### Polycaprolactone

15 Polycaprolactone used in the present invention may be any polycaprolactone, insofar as it is substantially non-tacky at room temperature (about 25°C), and it has crystallinity such that it can be molten by heating. Polycaprolactone may be (i) one obtained by polymerizing a starting material containing caprolactone, or (ii) one having recurring units obtained by ring opening polymerization of caprolactone.

20 In the case of an adhesive comprising the tackifying polymer and polycaprolactone, it is possible to substantially suppress the tackiness against the glass surface at room temperature by the crystallization of polycaprolactone. However, the adhesive can exhibit the desired level of adhesion force by pressing the adhesive to the glass surface at room temperature. When the higher adhesion force is required, the 25 adhesive may be heat pressed.

The melting point of polycaprolactone may depend on its molecular weight, and is usually in the range between 30 and 70°C, preferably in the range between 35 and 65°C, in particular in the range between 40 and 60°C.

30 The molecular weight of polycaprolactone may not be limited insofar as the adhesive can exhibit the desired adhesion force. In general, its weight average molecular weight is from 2,000 to 300,000, preferably from 5,000 to 250,000, in particular from 10,000 to 230,000. When the molecular weight is too small, the adhesion force to the

glass surface tends to decrease. When the molecular weight is too large, the compatibility of polycaprolactone with the tackifying polymer may deteriorate, so that the above-described intended effects may not be attained.

The adhesive of the present invention may contain a non-tacky polymer other than polycaprolactone, insofar as the effects of the present invention may not be impaired.

#### Tackifying polymer

The tackifying polymer used in the present invention is a polymer which is tacky at room temperature (about 25°C), and which is preferably compatible with the above-described polycaprolactone when it is heated to a temperature not lower than the melting point of polycaprolactone.

Whether the tackifying polymer is compatibilized with polycaprolactone when heated to a temperature not lower than the melting point of polycaprolactone can be determined with the clarity of the adhesive, that is, the change (decrease) of haze. For example, the transparency of a film adhesive (a film-form adhesive) consisting of the adhesive of the present invention and having a thickness of 30 to 60  $\mu\text{m}$  is compared between the heated state at a temperature not lower than the melting point of polycaprolactone and the state at room temperature (about 25°C) or less. At room temperature, polycaprolactone usually forms fine crystals and dispersed in the matrix comprising the tackifying polymer. Thus, the film adhesive has relatively high transparency, and the haze measured with a color difference meter is 5 % or more (usually 20 % or less). When polycaprolactone is molten and compatibilized with the tackifying polymer, the film adhesive becomes substantially transparent. If polycaprolactone is molten but is not compatibilized with the tackifying polymer, the haze does not substantially change. In such a case, the smaller haze means better compatibility. Accordingly, the haze of the film adhesive measured with the color difference meter is preferably 3 % or less, more preferably 2 % or less, when polycaprolactone and the tackifying polymer are in the compatibilized state.

The compatibility of polycaprolactone and the tackifying polymer can be simply judged by the transparency of a solution containing the two polymers. That is, one prerequisite for the good compatibility between the tackifying polymer and polycaprolactone is that a transparent mixture forms, when the first solution containing the

dissolved tackifying polymer and the second solution containing the dissolved polycaprolactone are mixed.

The compatibility of the two polymers can be confirmed by checking the transmission of polarized light with a polarization microscope. As is well known, when  
5 the polarization axes of a pair of polarizing plates are crossed at right angles, no light passes, so that the view becomes substantially dark.

A pair of polarizing plates, which are arranged so that their polarization axes are crossed at right angles, are observed with inserting the film adhesive made of the adhesive of the present invention between them. At room temperature, the fine crystals of  
10 polycaprolactone rotate the polarizing plane of the light entering the film adhesive, and thus the light is allowed to pass through the both polarization plates. Since the directions of the crystal axes are usually random, polycaprolactone contains the crystals which rotate the polarization plane of the light just 90 degrees to allow the light to pass through the both polarization plates, and also the crystals which hardly allow the light to pass through  
15 the polarization plates. As the fine crystals of polycaprolactone are smaller and better dispersed, they have the larger compatibility with the tackifying polymer. Accordingly, as the compatibility of the both polymers increases, the crystal size decreases, and thus the entire film in the field of view of the microscope (100 to 200 times magnification) is observed faintly bright. When the compatibility of the polymers is low, the crystal size  
20 becomes large, and thus the crystals can be observed as bright spots which are sprinkled on the dark background. When polycaprolactone is molten and becomes compatible with the tackifying polymer, the polymer mixture contained in the film adhesive is optically isotropic, and is darker than at room temperature.

In general, the tackifying polymer is a polymer having a hydroxyl group, a phenyl  
25 group, an alkyl group and a crosslinkable functional group.

The crosslinkable functional group means a functional group which can participate in the crosslinking reaction when the polymer is heated or irradiated with electromagnetic waves (including UV ray) or electron beams, and usually a functional group which reacts  
30 with the crosslinking component contained in the adhesive. Alternatively, the molecules of the tackifying polymer may be directly crosslinked through the crosslinkable functional groups. The details of the crosslinkable functional groups and the crosslinking component will be explained in detail.

One preferable example of the tackifying polymer used in the present invention is explained.

A preferable tackifying polymer is an acrylic polymer prepared by polymerizing a monomer mixture containing (A) a (meth)acrylic monomer having a hydroxyl group in the molecule, (B) a (meth)acrylic monomer having a phenyl group in the molecule, (C) an alkyl acrylate having 4 to 10 carbon atoms in the alkyl group and (D) a (meth)acrylic monomer having a crosslinkable functional group in the molecule. Such a polymer may be prepared by any conventional polymerization method such as solution polymerization.

Examples of the monomer (A) include 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxymethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl acrylate, etc.

As the monomer (A), one having both a hydroxyl group and a phenyl group in the molecule such as 2-hydroxy-3-phenoxypropyl acrylate is preferable. With such a monomer (A), the compatibility of the tackifying polymer with polycaprolactone is effectively improved.

Examples of the monomer (B) include those having a phenoxy group as a phenyl group such as phenoxyethyl acrylate, phenoxypropyl acrylate, etc.

Examples of the monomer (C) include n-butyl acrylate, isobutyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, etc. The monomer (C) has none of the above functional groups (the hydroxyl group, the phenyl group and the crosslinkable functional group).

As the monomer (D), unsaturated carboxylic acids such as (meth)acrylic acid; compounds having a thermally crosslinkable group such as epoxy group-containing (meth)acrylic monomers (e.g. glycidyl (meth)acrylate, etc.) and the like can be used. Furthermore, (meth)acrylic monomers having a unsaturated double bond and a photocrosslinkable functional group in the molecule are used to obtain a photocrosslinkable tackifying polymer. In this case, the monomer (D) having both a thermally crosslinkable group and a photocrosslinkable group may be used so that the tackifying polymer can be crosslinked with heat and light.

The proportion of the recurring units derived from the monomer (B) in the whole recurring units of the tackifying polymer is usually at least 0.5 mole %, preferably at least 1 mole %, in particular from 5 to 25 mole %. When the proportion of the recurring units derived from the monomer (B) is too low, the compatibility of the tackifying polymer with

polycaprolactone tends to decrease. When this proportion is too high, the press-adhesion property may deteriorate.

The proportion of the recurring units derived from the monomer (D) in the whole recurring units of the tackifying polymer is usually from 0.5 to 15 wt. %, preferably from 0.7 to 10 wt. %, in particular from 1 to 7 wt. %.

Besides the above acrylic polymers, examples of the tackifying polymer include nitrile-butadiene copolymers (NBR, etc.), styrene-butadiene copolymers (SBR, etc.), polyurethane, silicone polymers, etc. The tackifying polymers may be used singly or in admixture of two or more.

In addition to the polymers having the above essential functional groups, that is, the hydroxyl group, the phenyl group and the crosslinkable functional group, the tackifying polymer may be used in combination with a polymer which does not have such functional groups. However, the proportion of the polymers having the essential functional groups is at least 50 wt. %, preferably at least 60 wt. %, in particular at least 70 wt. %.

The molecular weight of the tackifying polymer used in the present invention is not limited insofar as the adhesive can exert the desired adhesion force. In general, the weight average molecular weight of the tackifying polymer is from 10,000 to 1,000,000.

A tackifier may be used together with the tackifying polymer, like in the case of conventional pressure-sensitive adhesives.

#### Crosslinkable functional groups

The crosslinkable functional group of the tackifying polymer is preferably a functional group other than the hydroxyl group, which is reactive with the thermally crosslinking component. Preferably, the tackifying polymer has at least one of a carboxyl group and an epoxy group as the crosslinkable functional group, while it may have both of them.

In such a case, a preferred thermally crosslinking component is compound having at least two crosslinkable functional groups reactive with the carboxyl group and/or the epoxy groups of the tackifying polymer. Such a compound is usually a monomer or an oligomer.

Examples of the combination of the crosslinkable functional group and the thermally crosslinkable component are as follows:

(1) When the crosslinkable functional group is the epoxy group, the thermally crosslinking component is preferably a bisamide crosslinking agent or an epoxy resin.

5 (2) When the crosslinkable functional group is the epoxy resin, the thermally crosslinking component is preferably a rosin having a carboxyl group in the molecule (carboxyrosin).

10 Either the carboxyl group or the epoxy group can effect the thermal crosslinking without deteriorating the compatibilizing effects of the hydroxyl group and the phenyl group of the tackifying polymer with polycaprolactone. In addition, it is easy to achieve the sufficient crosslinking degree for the increase of the heat stability and the effect to prevent the adhesive leavings by the thermal crosslinking reaction.

15 In the case of the above (1), carboxyrosin may be used together, while in the case of the above (2), the epoxy resin and/or the bisamide crosslinking agent may be used together.

#### Crosslinking components

20 The epoxy resin reacts with the carboxyl group of the tackifying polymer and functions to thermally crosslink the tackifying polymer. Examples of the epoxy resin include bisphenol A epoxy resins, bisphenol F epoxy resins, cresol-novolak epoxy resins, phenol-novolak epoxy resins, etc.

The epoxy equivalent of the epoxy resin is usually from 70 to 400, preferably from 80 to 300.

25 As the bisamide crosslinking agent, bisaziridine derivatives of dibasic acids such as isophthaloyl bis(2-methylaziridine) may be used. The bisamide crosslinking agent is particularly preferable since it can react with the tackifying polymer having the carboxyl group at room temperature and easily achieves the sufficient crosslinking degree.

30 When the tackifying polymer has the epoxy group in the molecule, preferable crosslinking components are carboxyrosins. The carboxyrosins have the carboxyl group in the molecule and react with the tackifying polymer. Thus, they function to thermally crosslink the tackifying polymer. As the carboxyrosin, gum rosin, wood rosin, tall oil rosin, and their chemically modified products (e.g. polymer rosin, etc.) may be used.

The carboxyrosins may be used singly or in admixture of two or more. Rosins having substantially no carboxyl group may be used together insofar as the effects of the present invention are not impaired.

When the above-described crosslinking component is used, the proportion of the crosslinking component in the whole adhesive (whole weight) is usually from 1 to 30 wt. %, preferably from 2 to 25 wt. %.

A reaction accelerator for the crosslinking component such as an epoxy resin may be compounded in the adhesive. Thereby, the thermal crosslinking conditions may be made mild.

The crosslinking components are not limited to those described above, and any other crosslinking component may be selected according to the kinds of the crosslinkable functional groups, crosslinking conditions, etc.

#### Preparation of adhesive

The adhesive of the present invention may be prepared by uniformly mixing the raw materials by a conventional mixing method. For example, the tackifying polymer, polycaprolactone, the crosslinking agent, the solvent, etc. are mixed with a mixing apparatus such as a homomixer, a planetary mixer, etc. to homogeneously dissolve or disperse the materials to obtain a liquid composition.

Such a liquid adhesive can be prepared in the form of a precursor solution containing the tackifying polymer and polycaprolactone by mixing the first solution comprising the dissolved tackifying polymer and the second solution comprising dissolved polycaprolactone. Then, the precursor solution is dried to obtain the adhesive consisting of the dried material of the precursor solution. In such a way, it is possible to form a specific morphology (interlinked structure) of crystalline polycaprolactone and the tackifying polymer having good compatibility with polycaprolactone, and thus the above-described properties (non-tackiness at room temperature and high adhesion force) can be most effectively achieved. When the crosslinking component is added, the third solution comprising the crosslinking component is added to the precursor solution.

For example, the above-prepared precursor solution is applied on a substrate and dried to form a film adhesive (or an adhesive layer) comprising the adhesive for glass. The tackifying polymer in the adhesive may be crosslinked in this step. The crosslinking

is carried out by aging the adhesive at room temperature for a specific time, or by applying heat or radiation.

As application means, conventional tools such as knife coaters, roll coaters, die coaters, bar coaters, etc. may be used.

5 As the substrate, a releasable substrate such as a liner, a substrate for an adhesive sheet (support), etc. may be used.

The drying of the applied precursor solution is usually carried out at a temperature of 60 to 180°C. The drying time is usually from several ten seconds to several minutes.

The thickness of the film adhesive is usually from 5 to 1,000 µm, preferably from  
10 10 to 500 µm, in particular from 15 to 100 µm.

The film adhesive according to the present invention can be used as an adhesive layer of an article to be adhered to glass, such as an adhesive sheet.

#### Article to be adhered to glass

15 An article to be adhered to the glass according to the present invention comprises an article body and an adhesive layer comprising the above-described adhesive, which is placed on one surface of said article body. Such an article can be adhered to the glass as an adhering surface by press adhering said adhesive layer to the adhering surface with pressing the article body against the adhering surface.

20 Examples of the article bodies include parts such as electronic parts, machine parts, optical parts, etc., and substrates for adhesive sheets, and so on.

The adhesive layer comprising the above-described adhesive has substantially no tackiness at room temperature. Thus, it has good slidability, and therefore the positioning of the adhesive sheet in relation to the glass surface is very easy in the adhering process.

25 In the meantime, after the positioning, the adhesive can be fixed to the adherent by simply pressing. The adhesive sheet, which can be easily positioned and press adhered, is preferably used as an adhesive sheet having a relatively large area (in general, at least 400 cm<sup>2</sup>) (e.g. interior or exterior decorative sheets), or relatively large-size retroreflective sheets for marking. Furthermore, The adhesive sheet of the present invention can be used  
30 as an application tape or film, since it can be peeled off at any time by heating without the adhesive leavings.



As the substrate of the adhesive sheet, any conventionally used substrate (support), for example, paper, metal films, polymer films, etc. may be used.

Examples of the polymers of the polymer films include polyimide, polyvinyl chloride, acrylic polymers, polyesters (e.g. polyethylene terephthalate, etc.), polyurethane,  
5 polyolefin polymers (including ethylene copolymers), and so on.

The substrate may be one allowing visible light or UV rays to transmit therethrough, or one reflecting light like a retroreflective sheet. Also, the substrate may be colored or decorated by printing, etc. In such cases, the adhesive sheet having the adhesive layer of the adhesive of the present invention is useful as a decorative sheet or a  
10 marking film.

The adhering surface of the adhesive layer is usually protected with a liner. The liner may be made of a paper sheet, a plastic film, or a laminate of a paper sheet and a plastic film.

In the case of the thermally easy-peeling adhesive sheet, the adhesion between the  
15 adhesive layer and the substrate is preferably as strong as possible. If the adhesion between the adhesive layer and the substrate is weak, a part or whole of the adhesive layer is left on the adhering surface of the adherent, when the adhesive sheet is peeled off from the adherent. To increase the adhesion between the adhesive layer and the substrate, a primer is applied to the surface of the substrate on which the adhesive layer is placed.

20 Preferably, the polymer constituting the substrate film comprises at least one of polyurethane and an ethylene-acrylic acid copolymer, since such a polymer film can be strongly adhered to the adhesive layer of the adhesive of the present invention without the use of a primer.

The thickness of the substrate is usually from 5 to 500  $\mu\text{m}$ , preferably from 10 to  
25 300  $\mu\text{m}$ , and the thickness of the adhesive layer is usually from 10 to 500  $\mu\text{m}$ , preferably from 15 to 300  $\mu\text{m}$ , in particular from 20 to 100  $\mu\text{m}$ .

Furthermore, the adhesive layer may contain any one of conventional additives, insofar as the effects of the present invention are not impaired. Examples of such additives include viscosity modifiers, defoaming agents, leveling agents, UV ray  
30 absorbers, antioxidants, pigments, fungicides, elastic fine particles of tacky or non-tacky rubbery polymers, tackifiers, catalysts to accelerate the crosslinking reaction, etc.

When the article is thermally peeled off after it is adhered to the glass surface, it is usually heated at a temperature of 60 to 120°C for 30 seconds to 5 minutes. Since the adhesive layer of the adhesive according to the present invention is used, the easy-peeling time lasts at least 5 minutes after the heating to peel the adhesive sheet.

- 5            Preferably, the easy-peeling condition may be maintained even when the adherent and the adhesive layer are cooled to room temperature (about 25°C), but the adhesion force (peel strength) again increases after 15 minutes from cooling to finish the readhesion.

10           In the course of the thermal peeling, the adherent and/or the adhesive sheet may be heated with a heating apparatus such as an iron, a drier, an IR (far IR) lamp, etc. When the substrate comprises a metal foil, the adhesive sheet may be heated by an electromagnetic induction heating method. Furthermore, the adherent and/or the adhesive sheet may be heated with a heat transfer medium such as a liquid or steam.

15           The peel strength of the adhesive sheet prior to heating for peeling off is usually at least 8 N/25 mm, preferably from 10 to 40 N/25 mm, in particular from 12 to 35 N/25 mm, when it is measured by the 180 degrees peeling test at a peeling rate of 300 mm/min. When the peel strength prior to the thermal peeling process is too low, the adhesive sheet may not be used in the same way as conventional adhesive sheets. When the peel strength prior to the thermal peeling process is too high, the peel strength in the thermal peeling  
20           process is too high, and thus the easy-peeling properties may not be improved.

            An optimum range of the peel strength in the thermal peeling process can be suitably selected according to the mechanical strength of the substrate (e.g. elastic modulus, elongation at break, etc.), peeling conditions (e.g. peeling rate), and so on. From the viewpoint of quick peeling, the peel strength is preferably 16 N/25 mm or less, when it  
25           is measured by the 180 degrees peeling test at a peeling rate of 300 mm/min.

            As can be seen from the above explanations, the above-described adhesive sheet (1) achieves the easily peelable state by heating it to a specific temperature to decrease the peel strength to a value smaller than that prior to heating, on a desired occasion after it is adhered to the glass surface, (2) can maintain such an easily peelable state for a certain  
30           period of time, (3) can be peeled off without leaving the adhesive on the adherent, and (4) can be easily readhered to an adherent (including other adherent) after peeling.

## Examples

### Example 1

The adhesive of this Example was prepared as follows:

5 An adhesive solution was prepared by mixing a solution containing a tackifying polymer, which was produced as described below (solvent: a mixture of 85 wt. % of ethyl acetate and 15 wt. % of methyl ethyl ketone; nonvolatile concentration: 30 wt. %), a solution of undermentioned polycaprolactone in toluene (nonvolatile concentration: 35 wt. %) and isophthaloyl bis(2-methylaziridine) as a thermally crosslinking bisamide. The obtained mixed solution was transparent.

10 The adhesive solution was applied on the surface of a substrate and dried in an oven at 95°C for 5 minutes to form an adhesive layer consisting of the adhesive of this Example on the substrate. Then, a liner was laminated on the adhering surface of the adhesive layer facing an adherent to finish the adhesive sheet of this Example.

The thickness of the adhesive layer was 30  $\mu\text{m}$ .

15 The used substrate was a both surfaces-easy adhering PET film (D709 available from TEIJIN DUPONT, thickness = 50  $\mu\text{m}$ ). The liner was a PET liner having a silicone-releasing surface.

The proportions of these components were such that tackifying polymer:polycaprolactone:crosslinking component = 85:15:0.2 (weight ratio of the nonvolatiles).

20 The used polycaprolactone was PLACCEL<sup>®</sup> H7 (available from Daicel Chemical Industries, Ltd.; weight average molecular weight  $M_w$  = 220,000, melting point  $T_m$  = 60°C).

25 The tackifying polymer used was a copolymer prepared by solution polymerizing the monomer mixture containing (A) a monomer having a phenoxy group and a hydroxyl group in the molecule (2-hydroxy-3-phenoxypropyl acrylate (represented by HPPA; ARONICS<sup>®</sup> M-5700 available from TOAGOSEI Co., Ltd.), (B) a monomer having a phenoxy group in the molecule (phenoxyethyl acrylate (represented by PEA; BISCOAT<sup>®</sup> #192 available from OSAKA YUKIKAGAKU KOGYO KABUSHIKIKAISHA), (C) n-butyl acrylate (represented by BA) available from TOAGOSEI Co., Ltd.) and (D) acrylic acid (represented by AA; available from Wako Pure Chemical Industries, Ltd.) The ratio of PEA:HPPA:BA:AA in the tackifying polymer was 55:15:25:5.

A peel test was carried out by press adhering a test piece (150 mm x 25 mm) formed from the above adhesive sheet to a glass plate having a thickness of 3 mm at 20°C according to JIS Z 0237 8.2.3.

5 A 180 degree peel strength was measured with TENSILON at a peeling rate of 300 mm/min. along the lengthwise direction of the sample just after adhesion, and after 4 minutes and 212 hours from the adhesion.

As a result, the peel strength just after adhesion was 5 N/25 mm, and thus the peeling was very easy, and also repeeling and readhering were easy. However, the peel strength surprisingly quickly increased to 26 N/25 mm after 4 minutes from the adhesion  
10 and 27 N/25 mm after 212 hours from the adhesion.

#### Comparative Example 1

The peel test was conducted in the same manner as in Example 1 but using a commercially sold adhesive tape. As a result, the peel strength just after adhesion was 8  
15 N/25 mm just after adhesion, 11 N/25 mm after 4 minutes, and 10 N/25 mm after 212 hours.

The commercially sold adhesion tape used in this Comparative Example was SCOTCHTINT Fasara® SH2EMOSL (available from 3M, USA), which comprises an adhesive layer of an acrylic adhesive containing no polycaprolactone.

20 Comparing the results of Example 1 and Comparative Example 1, it is understood that the adhesive sheet of Example 1 can attain the adhesion strength in the level sufficient for the practical use as an adhesive sheet for glass.

#### Examples 2-6

25 An adhesive sheet was produced in the same manner as that in Example 1 except that an weight ratio of the tackifying polymer to polycaprolactone or/and the thickness of the adhesive layer were changed as shown in Table 1.

Then, the slidability, the ordinary adhesion strength and the adhesive leavings (removal cleanliness) of the adhesive sheet were evaluated by the methods described  
30 below. The results are shown in Table 1.

Table 1

	Tackifying polymer/ Polycaprolactone	Thickness of adhesive layer ( $\mu\text{m}$ )	Slida- bility	Ordinary adhesion strength (N/25 mm)	Adhesive leavings
Ex. 1	85/15	30	OK	28	OK
Ex. 2	95/5	8	OK	15	OK
Ex. 3	90/10	9	OK	14	OK
Ex. 4	85/15	10	OK	14	OK
Ex. 5	70/30	30	OK	10	OK
Ex. 6	60/40	30	OK	2	OK
C. E. 1		30	NG	9	OK
C. E. 2		30	NG	12	OK

### Comparative Example 2

With an adhesive sheet "SCOTCHCAL<sup>®</sup> SP4582" (available from 3M, USA), the  
 5 slidability, the ordinary adhesion strength and the adhesive leavings (removal cleanliness)  
 of the adhesive sheet were evaluated in the same manners as in the above Examples. The  
 results are shown in Table 1.

The above adhesive sheet had an adhesive layer comprising an acrylic adhesive  
 containing no polycaprolactone, which is different from the adhesive of the adhesive sheet  
 10 used in Comparative Example 1.

### Evaluation methods

#### Ordinary adhesion strength

A test piece (150 mm x 25 mm) formed from the adhesive sheet of each example  
 15 was press adhered to the above described glass plate at 20°C according to JIS Z 0237  
 8.2.3.

Then, a 180 degree peel strength was measured with TENSILON at a peeling rate  
 of 300 mm/min. along the lengthwise direction after maintaining the sample at 20°C for  
 48 hours from the adhesion, and used as an ordinary adhesion strength.

20

#### Slidability

At a temperature of 20°C, a test piece was placed on the glass plate so that the  
 adhesion surface of the adhesive layer was in contact with the glass surface. Then,

whether the test piece could be easily moved horizontally or not was evaluated with the hand feeling. When the test piece could be slid with substantially no resistance, it was ranked "Good (OK)", while when the sliding was difficult due to the high resistance caused by adhesion to the adherent, it was ranked "No good (NG)".

5

#### Adhesive leavings

The surface of the glass plate was visually evaluated after the peel strength test in the heat peel mode. When no adhesive leavings were observed, it was ranked "Good (OK)", and when the adhesive leavings were partially observed, it was ranked "Normal (NG)".

10

From the above results, the following can be understood:

The adhesive sheets of Examples 1-5 had good slidability, and had a high adhesion strength of 10 N/25 mm or more after 48 hours and few adhesive leavings. The adhesive sheet of Example 6 could be peeled off with a small force even after 48 hours, and thus

15

used as an adhesive for glass having permanent easy-peeling properties.

The adhesive sheets of Comparative Examples 1 and 2 comprising the adhesive layers containing no polycaprolactone had low slidability.

#### Example 7

20

An adhesive sheet of this Example was prepared in the same manner as in Example 2 except that polycaprolactone was changed to PLACCEL<sup>®</sup> HIP (available from Daicel Chemical Industries, Ltd.; weight average molecular weight  $M_w = 25,000$ , melting point  $T_m = 60^\circ\text{C}$ ) and the composition of the tackifying polymer was changed to a ratio of PEA:HPPA:BA:AA = 30:15:50:5. Then, the easiness of thermal peeling of the adhesive

25

sheet was evaluated as follows:

The peel test was conducted in the same manner as in the evaluation of the ordinary adhesion strength except that the adhered adhesive sheet was heated prior to peeling. The heating was carried out by blowing a hot air with an industrial drier onto the substrate surface of the test piece to heat the test piece to about  $100^\circ\text{C}$ . After

30

The thermal peel strength was 14 N/25 mm.

The ordinary peel strength measured in the same manner as above except that the test piece was not heated prior to peeling was 18 N/25 mm.

From the above results, the adhesive for glass according to the present invention can be easily peeled off by the thermal peeling operation without leaving the adhesive  
5 with a smaller peeling force than the ordinary adhesion strength (decreased by 20 % in the Example), even after 5 minutes from heating.

We claim:

1. An adhesive for glass which is used to be press adhered to a glass surface  
5 as an adherent comprising a crosslinked tackifying polymer and polycaprolactone,  
characterized in that said tackifying polymer is a polymer obtained by polymerizing a  
monomer mixture containing
  - (a) a monomer having a hydroxyl group in the molecule,
  - (b) a monomer having a phenyl group in the molecule,
  - 10 and
  - (c) a monomer having a C<sub>4</sub>-C<sub>10</sub> alkyl group in the molecule.
2. The glass adhesive according to claim 1, wherein said adhesive further  
comprises a crosslinking component, said monomer mixture further comprises (d) a  
15 monomer having a crosslinkable functional group reactive with said crosslinking  
component in the molecule, and said tackifying polymer is crosslinked through the  
reaction of said crosslinking component and said crosslinkable functional group.
3. The glass adhesive according to claim 1, wherein the total amount of said  
20 monomer (a) and (b) is from 42 to 90 wt. % based on the whole weight of said monomer  
mixture, and the amount of said monomer (c) is from 9 to 55 wt. % based on the whole  
weight of said monomer mixture.
4. An article to be adhered to glass comprising an article body and an  
25 adhesive layer comprising an adhesive according to claim 1 which is placed on one  
surface of said article body, wherein said article can be adhered to the surface of glass as  
an adhering surface by press adhering said adhesive layer to said adhering surface with  
pressing said article body against said adhering surface.



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(54) Title: GLASS ADHESIVE AND ARTICLE TO BE ADHERED TO GLASS

(57) Abstract: To provide an adhesive for glass, which is particularly suitable for adhering an article to a glass surface as an adhering surface, exhibits good slidability without the use of detackifying particles, and has removal cleanliness after the completion of adhesion. An adhesive for glass which is used to be press adhered to a glass surface as an adherent, which contains polycaprolactone and a crosslinked tackifying polymer obtained by polymerizing a monomer mixture containing a monomer having a hydroxyl group in the molecule, a monomer having a phenyl group in the molecule, and a monomer having a C4-C10 alkyl group in the molecule.

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## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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WPI Data, PAJ, EPO-Internal

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☒ Further documents are listed in the continuation of box C☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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